NMR Relaxation and novel NMR Cryoporometry studies of clathrate formation and dissolution in vapour/water/ice/hydrate systems.

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CENTRE FOR GAS HYDRATE RESEARCH

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Abstract

We have measured the T_2 relaxation time of water/ice systems in SBA-15 porous silica, and believe this to be a **novel observation of ice in a plastic (or rotator) phase**. The **brittle-crystal to plastic phase-transition** and **plastic to liquid phase-transition** have also been observed using NMR Cryoporometry.

Relaxation time measurements of bulk water/ice/hydrate systems also show a long T_2 component that indicates the probable existence of a rotator phase. In both these systems the long T_2 component reversibly converts to brittle ice at lower temperatures.

Equilibrium phase transitions on a cooling ramp are frequently obscured by metastable super-cooling. **A novel 4 ramp Cryoporometry protocol has been developed** that enables measurements to be made of both the equilibrium Gibbs-Thomson depressed freezing and melting phase transitions. This has enabled measurements to be made that have an environmental impact :

Environmental Impact :

Hydrate dissolution temperature : is lowered if the hydrate is in a pore — this can change the marine hydrate calculated layer thickness by 30 to 100m.

Hydrate formation temperature : A far lower sea temperature is needed to re-form the hydrate once dissociated.

NMR Relaxation in water/ice systems in SBA-15.

Water/Ice in SBA-15 nanopores exhibits a relaxation component with a T_2 of 100 - 200μs over a wide temperature range. This is due to the onset of rotation motion around 200-220K, indicating that **the ice is in a plastic (or rotator) phase**.

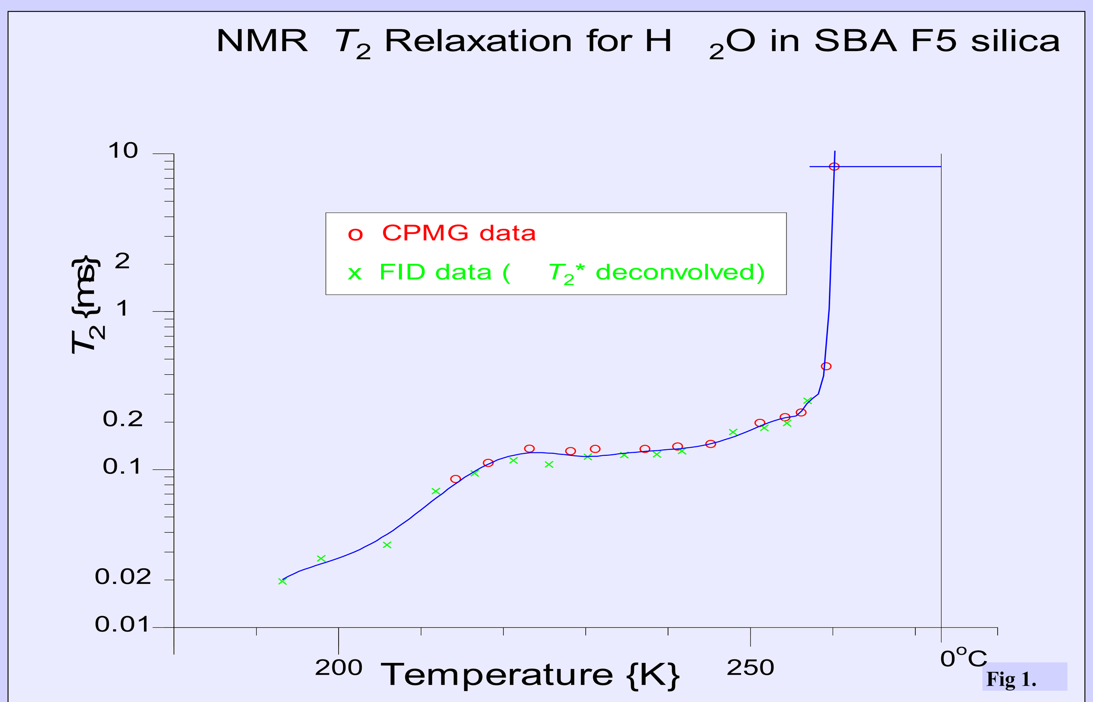

Fig 1.

Brittle-Plastic Phase Transitions in Water./Ice

NMR Cryoporometry

Brittle to Plastic and Plastic to Water phase transitions as observed by H_2O Cryoporometry in SBA-15 nanopores.

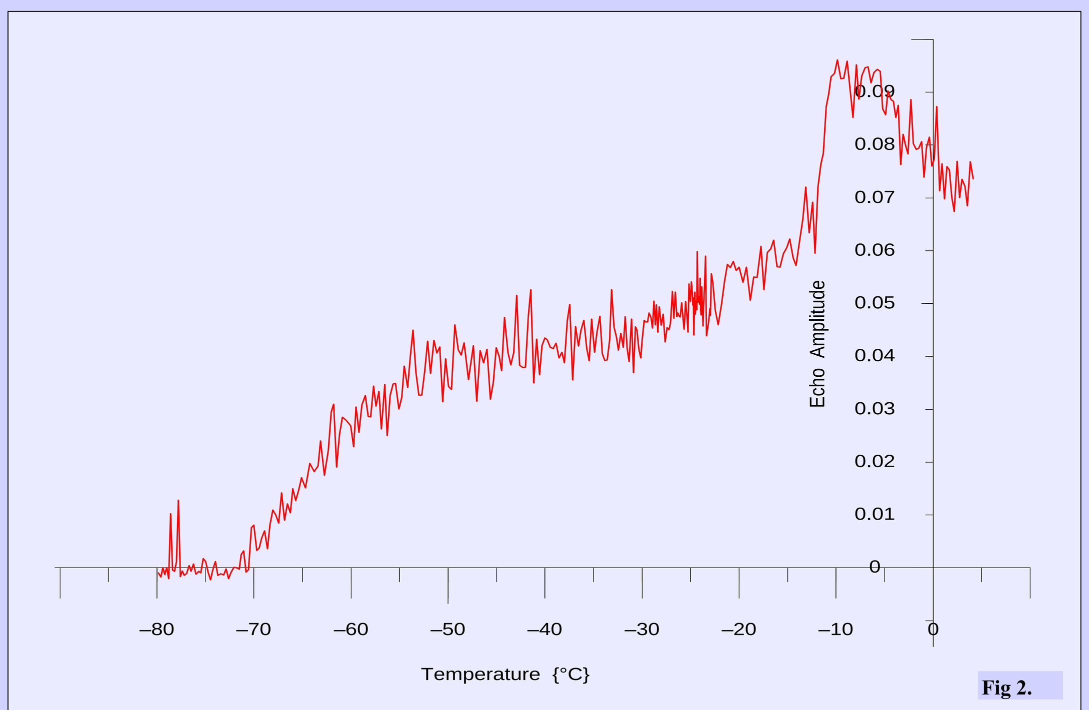

Fig 2.

NMR Relaxation in bulk hydrate (clathrate) systems.

Hydrates : can form at temperatures above or below the freezing point of water, and consist of a gas or liquid trapped in a cage of water molecules (figure 3).

1 volume of hydrate can accommodate up to 175 volumes of gas.

Hydrate plugs can block oil and gas pipelines.

There are large deposits of methane hydrates on the bottom of the sea floor—possible fuel reserves, but they also act to stabilize sub-sea sediment slopes.

There is an interest in storing waste CO_2 beneath the sea bed, both as hydrates and as gas trapped beneath the hydrate layer.

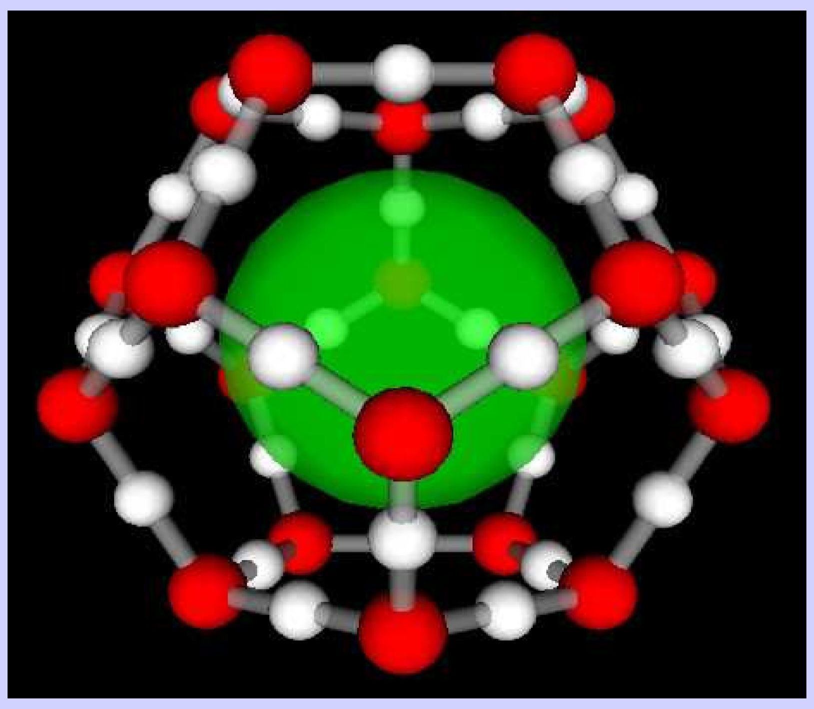

Fig 3.

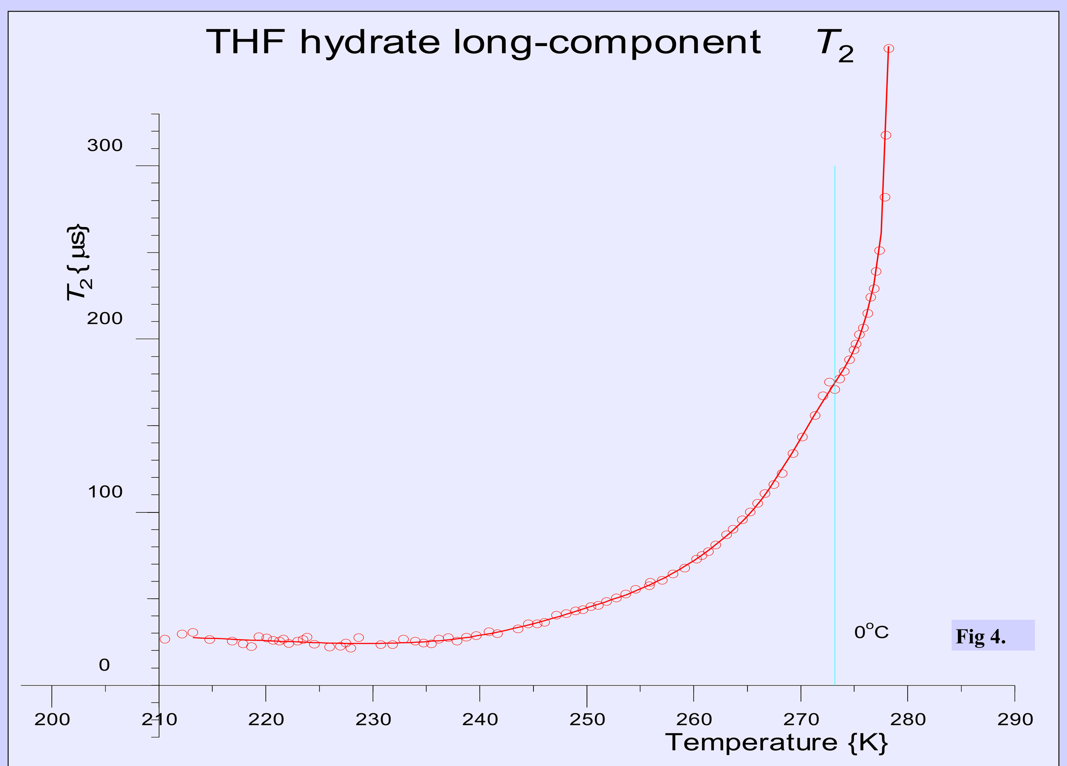

Fig 4.

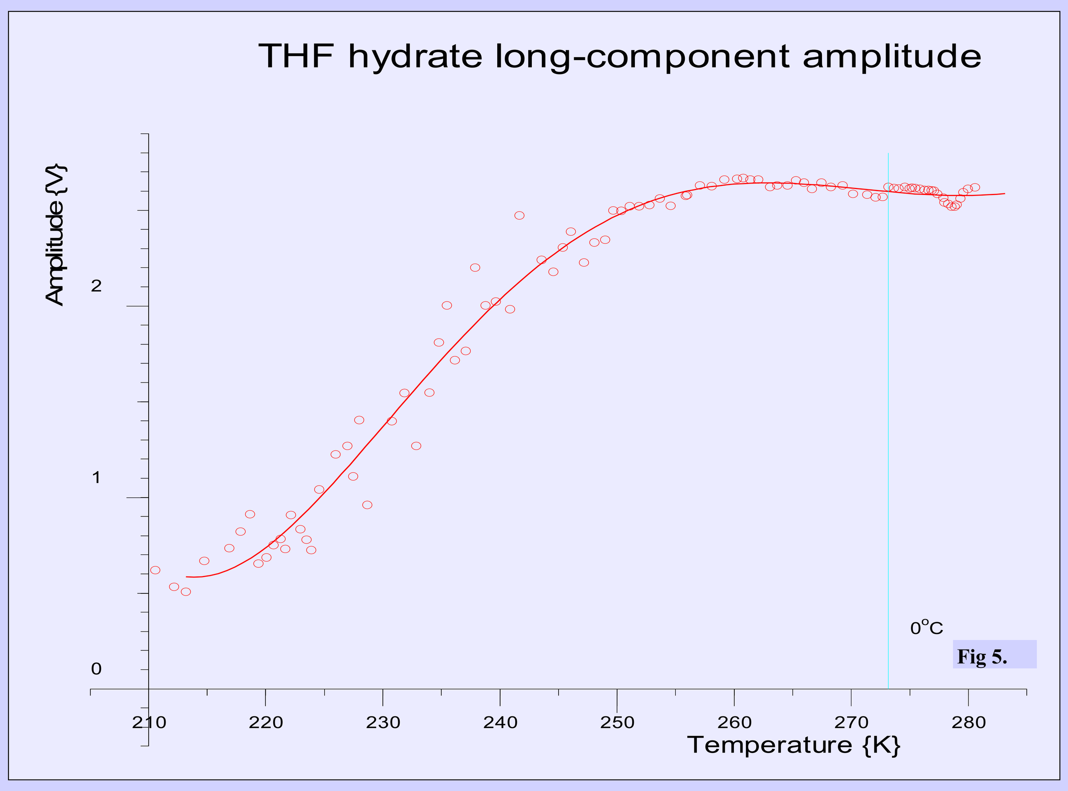

Fig 5.

NMR Cryoporometry in hydrate (clathrate) systems in CPG (B) porous silica.

A Novel 4-ramp Cryoporometry protocol was used to observe both the dissolution and formation events for Tetrahydrofuran hydrate in CPG (B) mesopores, thus avoiding the obscuring effect of the metastable supercooling that occurs in these systems.

This data shows that while the hydrate dissociation temperature is lowered by 2°C in these CPG mesopores, the association temperature is lowered by 7.4°C, which would require a much larger change in sea temperature in a marine environment before hydrates could again form.

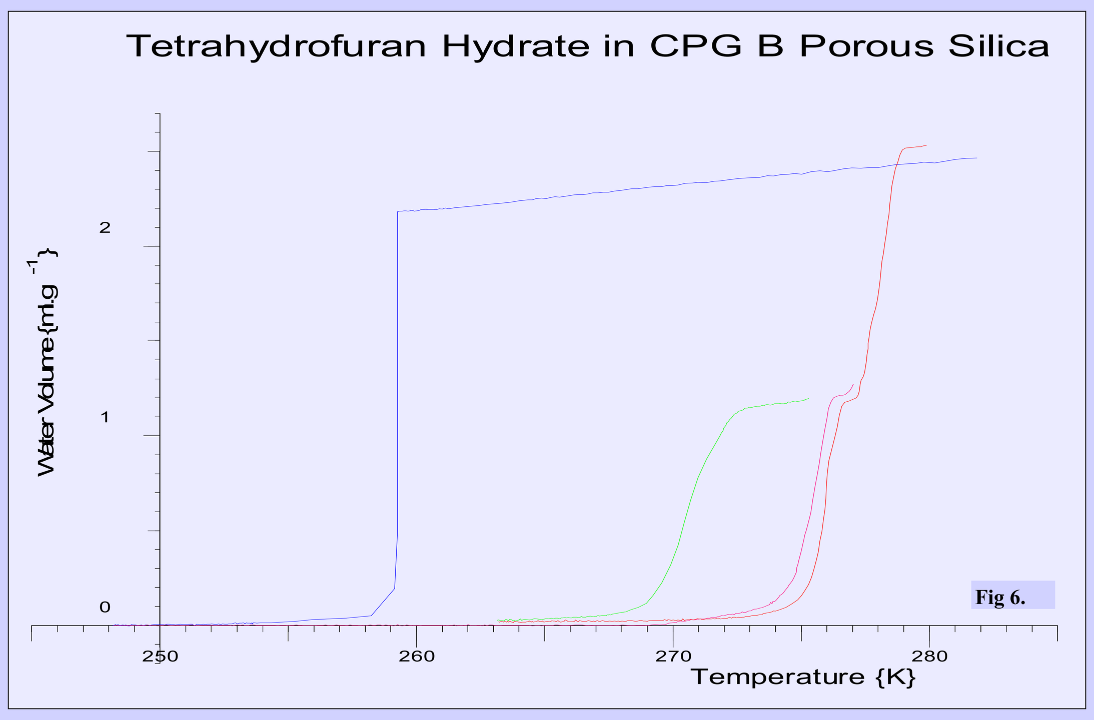

Fig 6.

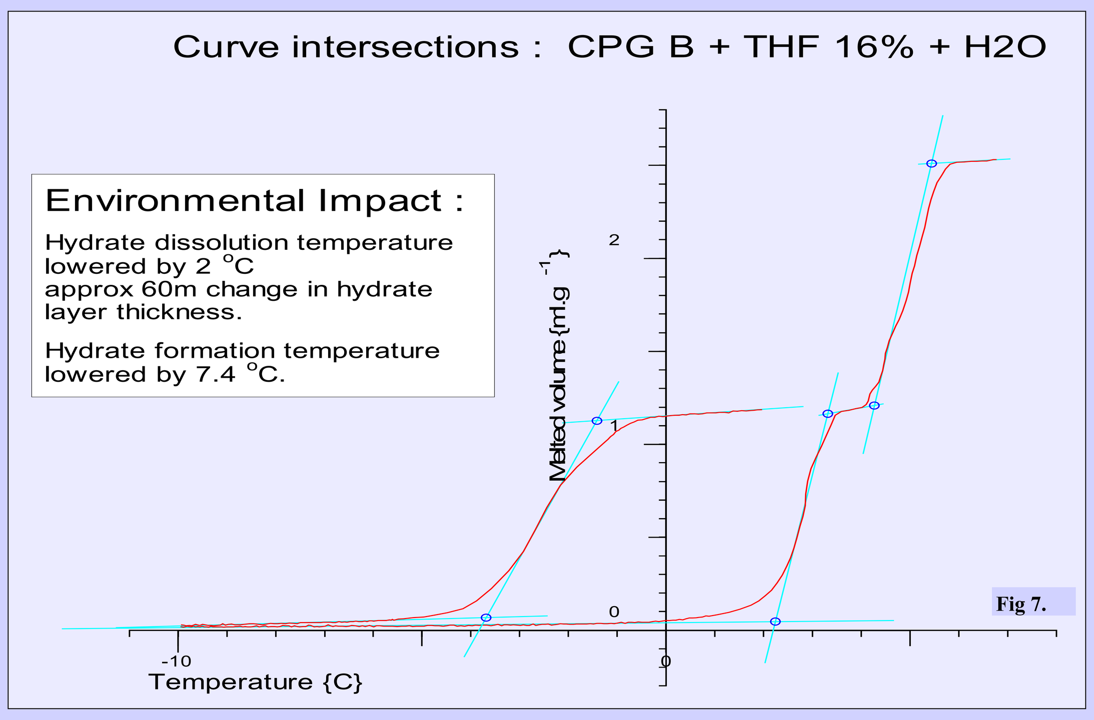

Fig 7.

Conclusions

1) Ice in confined geometry and near surfaces shows a much longer T_2 than brittle ice. This is believed to be **a novel observation of ice in a plastic phase**.
2) Liquid hydrate systems in the bulk show a much higher mobility than brittle ice and may be plastic.
3) In both these systems the long T_2 component reversibly converts to brittle ice at lower temperatures.
4) **Hydrate dissolution temperature** is lowered if the hydrate is in a pore.
5) **Hydrate formation temperature** in a pore is lowered to a much greater extent.
6) These measurements have an impact on the behaviour of hydrate systems in marine sediments.